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ABSTRACT

This booklet, one of a series of 17 developed at Prince George's Community College, Largo, Maryland, provides an individualized, self-paced undergraduate organic chemistry instruction module designed to augment any course in organic chemistry but particularly those taught using the text "Organic Chemistry" by Morrison and Boyd. The entire series of modules covers the first 13 chapters of the Morrison-Boyd text in great detail. Each module has been provided with from one to three audio tapes, available from Prince George's Community College, to provide students additional explanations of particular concepts. Each module includes a self-evaluation exercise, a reference guide, worksheets to be completed with the audiotapes, answer sheets for the worksheets, a progress evaluation, an answer sheet for the progress evaluation, an answer sheet for the self-evaluation exercise, an introduction to the topic covered by the module, and student performance objectives for the module. The topic of this module is arenes. (SL)

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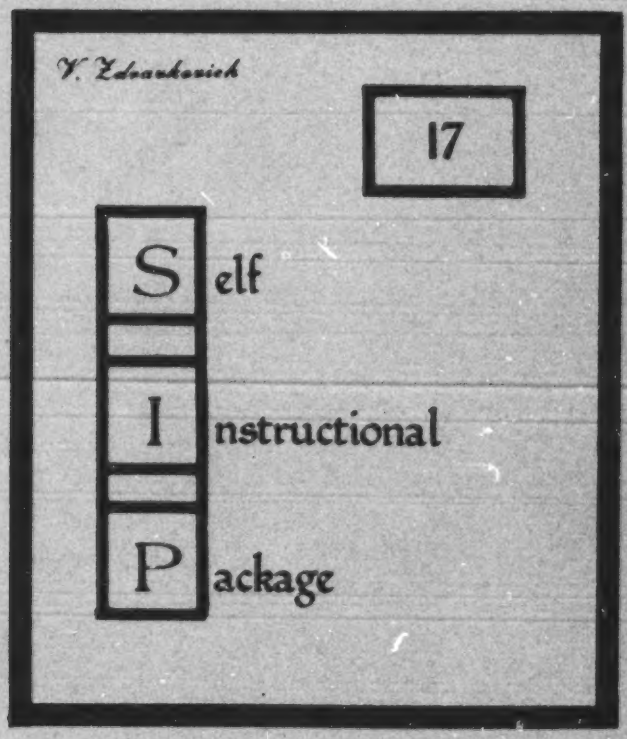


ARENES

V. Zdravkovich

SE 021 588

Self Instructional Sequence in

ORGANIC CHEMISTRY

"Copr.," V. Zdravkovich 1975

Self Instructional Package No. 17
Form A - List of Objectives

ARENES

I. Friedel Crafts Reactions

The student will be able to write the step-by-step mechanism for the Friedel Crafts alkylation and acetylation reactions.

The student will be able to identify the limitations of the Friedel Crafts alkylation reaction and apply them to specific problems.

II. Mechanisms

The student will be able to write the step-by-step mechanism for:

a) different electrophilic aromatic substitution reactions of arenes.

b) free radical halogenation of arenes.

c) different electrophilic addition reactions of alkenylbenzenes.

d) different free radical addition reactions of alkenylbenzenes.

e) different free radical and carbonium ion reactions of aryl dienes.

The student will be able to explain the preferred orientation in the different reactions of arenes on the basis of their mechanism.

III. Reaction of arenes

The student will be able to write the structural formula of the benzylic free radical, triphenyl methyl free radical, and the benzylic carbonium ion and explain their unusual stability in terms of:

a) orbital picture concept and b) concept of resonance.

The student will be able to write all the resonance structures of the benzylic free radical and of the benzylic carbonium ion.

The student will be able to draw the structure and name the products in the reactions of an arene with nitrating mixture, hot KM_nO_4; Br_2,light; Br_2,Fe; $Tl(OOCCF_3)_3$,CF_3COOH; H_2SO_4,SO_4; Friedel Crafts alkylating and acylating reagents.

The student will be able to draw the structure and name the products in the reactions of an alkenyl benzene with: H_2O, acid; hot KM_nO_4; KM_nO_4,aq; CHX_3, ROOR, hv; CX_4, ROOR,hv acid; peroxide, light; Br_2,CCl_4; Br_2,hv; H_2,Pt; HX; HBr, ROOR, hv.

The student will be able to identify all the steps in the laboratory synthesis of different alkyl benzenes, alkenyl benzenes, alkynyl benzenes and their derivatives starting from benzene.

The student will be able to identify (i.e. draw the structure and name) all the intermediate compounds in the different multisynthetic schemes.

Self Instructional Package No. 17
Form B - Self Evaluation Exercise

ARENES

Identify the statements below as True or False by placing a capital T or F in the space provided to the left.

1. _____ Benzylic free radical is unusually stable because of the resonance structures.

2. _____ The delocalization of the odd electron over two rings is the reason for the unusual stability of the diphenyl methyl free radical.

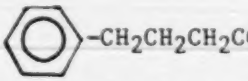
3. _____ In the benzyl carbonium ion, the clouds encompass seven p atomic orbitals and contain six electrons.

4. _____ The major product in the reaction of phenyl propane with bromine in light is 1-phenyl-2-bromo propane due to the great stability of the benzylic free radical.

5. _____ The relatively high stability of the benzylic carbonium ion is due to the delocalization of the positive charge over the ring.

6. _____ Reaction of benzene with dichloromethane in presence of $AlCl_3$ will yield mainly diphenylmethane.

7. _____ Reaction of n-butyl benzene with hot $KMnO_4$ will yield:



(4-phenyl butanoic acid)

8. _____ Aniline undergoes Friedel-Crafts alkylation reaction readily due to the unpaired electrons on nitrogen.

9. _____ Nitrobenzene does not undergo Friedel-Crafts alkylation reaction.

10. _____ Triphenyl methyl free radical is more stable than the benzylic free radical.

Circle the correct answer or answers in the questions below:

11. The major product in the reaction of 1-phenyl-propene with HBr is:

a) 1-phenyl-2-bromo propane
b) 3-bromo-1-phenyl propene
c) 1-phenyl-1-bromo propane
d) 3-bromo-1-phenyl propane

12. The major product in the reaction of 1-phenyl propane with bromine in presence of light is:

    a) o-bromo propyl benzene
    b) p-bromo propyl benzene
    c) 1-phenyl-1-bromo propane
    d) 1-phenyl-2-bromo propane

13. The correct steps in the laboratory synthesis of 1-phenyl-3-bromo propane from benzene are:

    a) $CH_3CH_2\overset{O}{\overset{\|}{C}}Cl, AlCl_2$; Zn(Hg)acid; Br_2,hv; KOH; Br_2,hv; H_2,Pt

    b) $CH_3CH_2\overset{O}{\overset{\|}{C}}-Cl, AlCl_3$; Zn(Hg) acid; Br_2,hv; KOH, HBr

    c) $CH_2Br\ CH_2\ \overset{O}{\overset{\|}{C}}\ Cl$, $AlCl_3$; Zn(Hg) acid

    d) $CH_3CH_2CH_2Cl$, $AlCl_3$; Br_2,hv; KOH; HBr, ROOR, hv

14. The correct steps in the laboratory synthesis of 1,4-diphenyl-1-bromo butane from benzene are:

    a) CH_3CH_2OH, acid, Br_2,hv; KOH; HBr,ROOR,hv; Na; Br_2,hv

    b) $CH_2(C_6H_5)CH_2\ CH_2\ \overset{O}{\overset{\|}{C}}-Cl$, $AlCl_3$; Zn(Hg)acid; Br_2,hv

    c) $CH_2\ Br\ CH_2\ CH_2\ \overset{O}{\overset{\|}{C}}-Cl$, $AlCl_3$; Zn(Hg)acid; benzene, $AlCl_3$; Br_2,hv

    d) $CH_3\ CH_2\ Cl$, $AlCl_3$; Na; Br_2,hv

15. The correct steps in the laboratory synthesis of 1,2-diphenyl-1,2-ethane diol from benzene are:

    a) CH_3Br, $AlCl_3$; Na; Br_2,hv; KOH; KM_nO_4,aq

    b) C_2H_5OH, acid; Br_2,hv; KOH; HBr, ROOR, hv; $AlCl_3$, benzene; Br_2,hv; KOH, KM_nO_4,aq

    c) $CH_2(C_6H_5)CH_2OH$, acid; Br_2,hv; KOH; KM_nO_4,aq

    d) $CH_3Cl\ BF_3$; Br_2,hv; Na; Br_2,hv; KOH; KM_nO_4,aq

SIP No. 17
Form B - Self Evaluation Exercise

16. The best way to prepare m-nitropropyl benzene is:

a) HNO_3, H_2SO_4; $CH_3\ CH_2\overset{O}{\overset{\|}{C}}-Cl$, $AlCl_3$; Zn(Hg) acid

b) $CH_3CH_2\overset{O}{\overset{\|}{C}}\ Cl$, $AlCl_3$; HNO_3, H_2SO_4; Zn(Hg) acid

c) $CH_3CH_2\ CH_2Cl$, $AlCl_3$; HNO_3, H_2SO_4

d) HNO_3, H_2SO_4; $CH_3\ CH_2\ Cl$, $AlCl_3$

17. The correct resonance structures which show the delocalization of the positive charge in the carbonium ion are:

I II III IV

a) I
b) II
c) III
d) IV

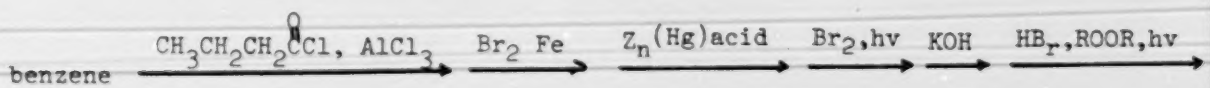
18. The product obtained in the multisynethetic scheme below is:

a) 1-o bromo phenyl-2-bromo butane

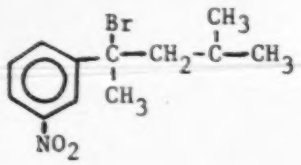
b) 1-m bromo phenyl -1-bromo butane

c) 1-p bromo phenyl-1-bromo butane

d) 1-m bromo phenyl-2-bromo butane



19. The correct IUPAC name assigned to the compound below is:



a) 2-bromo-2-benzyl-4-methyl pentane

b) m-nitrophenyl-2-bromo-4-methyl pentane

c) 2-bromo-2-m-nitrobenzyl-4-methyl pentane

d) 2-bromo-2-m-nitrophenyl-4-methyl pentane

Self Instructional Package No. 17
Form C - Reference Guide

ARENES

The Reference Guide should be used in conjunction with Form B or the Self Evaluation Exercise. The references give correlation between the questions in Form B and the available material in the textbook and in form of tapes.

Questions 1, 4	Chapter 12, Sections 13, 14
Questions 2, 10	Chapter 12, Section 15
Questions 3, 5, 17	Chapter 12, Section 18
Question 6	Chapter 12, Section 6
Question 7	Chapter 12, Sections 9, 10
Questions 8, 9	Chapter 12, Section 8
Question 11	Chapter 12, Sections 17, 18
Question 12	Chapter 12, Sections 12, 13
Questions 13, 14, 15, 16, 18	Chapter 12, Sections 5, 6, 9, 11, 16
Question 19	Chapter 12, Sections 1, 2

Additional explanations and examples for all questions are provided in the Tape - titled ARENES.

Self Instructional Package No. 17
Form D - Progress Check Evaluation

ARENES

Identify the statements below as true or false by placing a capital T or F in the space provided.

1. _____ 2-phenyl methyl free radical is more stable than the triphenyl methyl free radical.

2. _____ The relatively high stability of the benzyl carbonium ion is due to the electron releasing inductive effect of the carbon bearing the positive charge.

3. _____ Benzyl carbonium ion is more stable than the diphenyl methyl carbonium ion.

4. _____ The delocalization of the positive charge over the ring in the benzyl carbonium ion is the reason for its relatively high stability.

5. _____ Aniline does not undergo Friedel-Crafts alkylation reaction because of the high electron density on the ring.

6. _____ Benzoic acid readily undergoes Friedel-Crafts alkylation reaction.

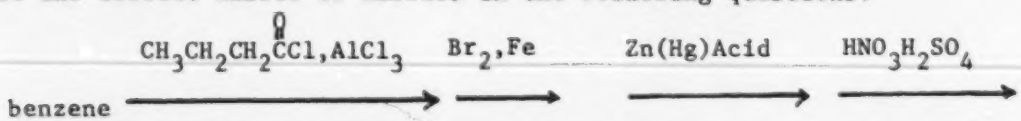
7. _____ Nitrobenzene does not undergo Friedel-Crafts alkylation reaction because of the deactivating effect of the nitro group.

8. _____ The resonance structures of the intermediate carbonium ion in the alkylation reaction show the positive charge to be concentrated in o, m, and p position relative to the alkyl group.

9. _____ The attacking species in the reaction of 1-chloro-2-methyl propane with benzene in presence of $AlCl_3$ is the t-butyl carbonium ion.

10. _____ Triphenyl methyl free radical is an example of a "long lived" free radical.

Circle the correct answer or answers in the following questions:



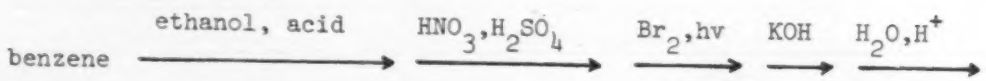
a) 2-nitro-3-bromo butyl benzene

b) 3-nitro-4-bromo butyl benzene

c) 3-bromo-4-nitro butyl benzene

d) 2-nitro-4-bromo butyl benzene

12. The product obtained in the multisynthetic scheme below is:



a) 1-m - nitrophenyl-2-ethanol

b) 1-m-nitrophenyl-1-ethanol

c) 1-o-nitrophenyl-1-ethanol

d) 1-p-nitrophenyl-1-ethanol

13. The reagents which will lead to the synthesis of 2-bromo-1-m-bromo phenyl propane are:

a) n-propylchloride, $AlCl_3$; Br_2,Fe; Br_2,hv; KOH; HBr

b) $CH_3CH_2\overset{O}{\overset{\|}{C}}Cl$, $AlCl_3$; Br_2,Fe; Zn(Hg)acid; Br_2,hv; KOH; HBr,ROOR,hv

c) $CH_3CH_2CH_2OH$, acid; Br_2,hv; Br_2,Fe; KOH; HBr

d) $CH_3CH_2\overset{O}{\overset{\|}{C}}Cl$, $AlCl_3$; Zn(Hg)acid; Br_2,Fe; Br_2,hv; KOH; HBr,ROOR,hv

14. The correct steps in the multisynthetic laboratory synthesis of polystyrene from benzene are:

a) ethylene, acid; Br_2,hv; KOH; peroxide, light;

b) ethylchloride, $AlCl_3$; Br_2,hv; KOH; acid

c) ethanol, acid; Br_2,hv; KOH; peroxide, light

d) 2-bromo-1-ethanol acid; KOH; acid

15. The correct choice and sequence of reagents required for the preparation of o-iodobenzoic acid are:

a) CH_3Cl, $AlCl_3$; hot KM_nO_4; $Tl(OOCCF_3)_3$ CF_3COOH; KI

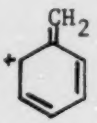
b) CH_3Cl, $AlCl_3$; I_2,Fe; hot KM_nO_4

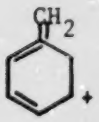
c) CH_3Cl, $AlCl_3$; $Tl(OOCCF_3)_3$ CF_3COOH; KI; KM_nO_4, hot

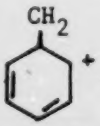
d) CH_3Cl, $AlCl_3$; hot KM_nO_4; I_2,Fe

16. The correct resonance structures of the benzyl carbonium ion are:

a)

c) 

b) 

d) 

17. The correct statements about the benzyl free radical are:

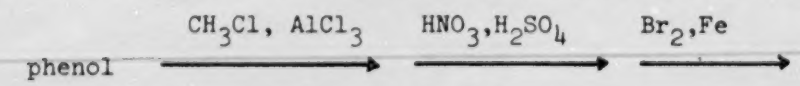
a) the unpaired electron is delocalized over seven carbon atoms.

b) the relatively high stability of this species results from the electron withdrawing effect of the ring.

c) a uniform cloud of π electron density containing seven electrons is formed.

d) the unpaired electron adjacent to the ring is stabilized through resonance.

18. The major product formed in the multisynthetic scheme below is:



a) 2-methyl-4-nitro-6-bromo phenol

b) 2-nitro-4-methyl-6-bromo phenol

c) 2-bromo methyl-4-nitro phenol

d) 3-nitro-4-methyl-6-bromo phenol

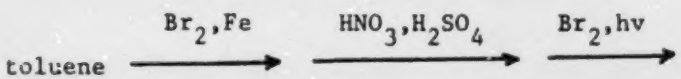
19. The major product formed in the multisynthetic scheme below is:

a) bromo-(3-nitro-4-bromo phenyl) methane

b) 2-nitro-4,6-dibromotoluene

c) 3-nitro-4,6-dibromotoluene

d) bromo-(2-nitro-4-bromo phenyl) methane



Self Instructional Package No. 17
Form B^1 - Self Evaluation Exercise - Answers

ARENES

1.	F	11.	c
2.	T	12.	c
3.	T	13.	a, c
4.	F	14.	a, b
5.	T	15.	b, d
6.	T	16.	b
7.	F	17.	a, b, c
8.	F	18.	d
9.	T	19.	d
10.	T		

Self Instructional Package No. 17
Form D^1 - Progress Check Evaluation - Answers

ARENES

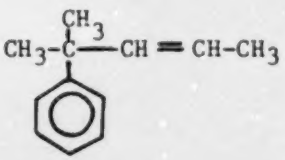
1.	F	11.	a, c
2.	F	12.	c, d
3.	F	13.	b
4.	T	14.	a, b, c, d
5.	F	15.	a
6.	F	16.	a, c
7.	T	17.	a, c, d
8.	F	18.	b
9.	T	19.	d
10.	T		

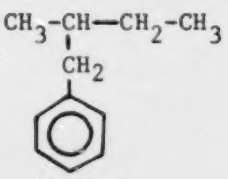
Self Instructional Package No. 17
Tape 1 - Work Sheet

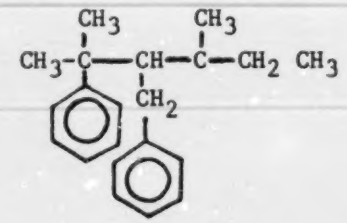
ARENES

Assignment No. 1 - Assign the correct IUPAC names to the following compounds:

a) $C_6H_5-C\equiv C-C_6H_5$

b) 

c) 

d) 

Assignment No. 2 - Draw the structure of the following compounds:

a) isopropylbenzene (cumene)

b) diphenyl methane

c) p-dibenzylbenzene

d) cyclohexyl benzene

e) 1,3-diphenyl-2,4-hexadiene

SIP No. 17
Tape 1 - Work Sheet

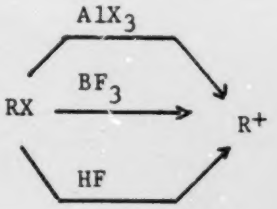
Example No. 1 - Friedel Crafts alkylation mechanism

Step I - Formation of the electrophile - alkyl carbonium ion

from an alcohol: $ROH \xrightarrow{acid} R^+$

from an alkene: $R\text{-}CH=CHR \xrightarrow{acid} R\text{-}CH_2\text{-}\overset{+}{C}HR$

from an alkyl halide

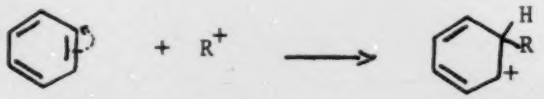


Step Ia - Possible rearrangement of the carbonium ion

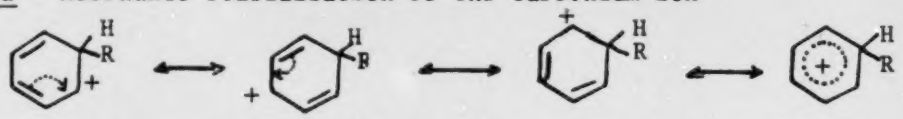
$1°\ R^+ \xrightarrow{\text{Hydride shift or methyl shift}} 2°R^+ \text{ or } 3°R^+$

$2°R^+ \xrightarrow{\text{Hydride shift or methyl shift}} 3°R^+$

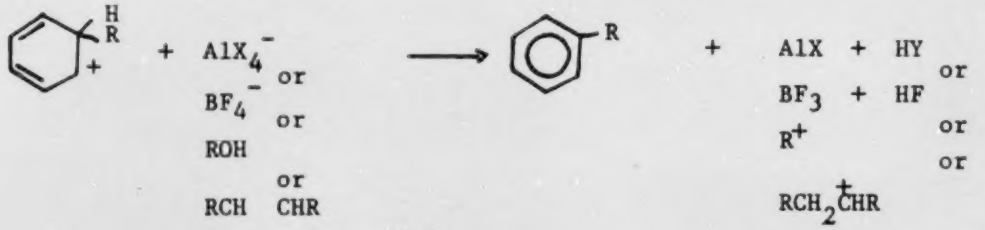
Step II - Attack of the electrophile on the benzene ring



Step IIa - Resonance stabilization of the carbonium ion



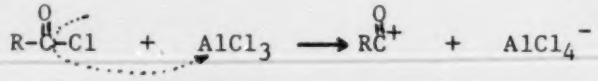
Step III - Recovery of the aromatic character and regeneration of the catalyst



SIP No. 17
Tape 1 - Work Sheet

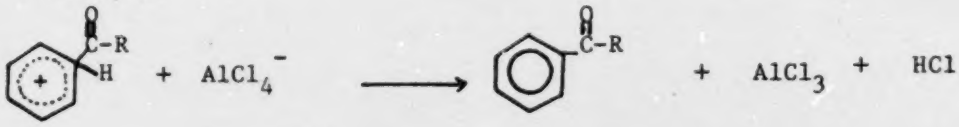
Example No. 2 - Friedel-Crafts acylation mechanism

Step 1 - formation of the electrophile - (acilium) ion



Step 2 - Attack of the electrophile on benzene ring

Step 3 - Recovery of the aromatic character and the regeneration of the catalyst



Example No. 3 - Limitations of the Friedel-Crafts alkylation reaction

1. Rearrangement of the carbonium ion.
2. Polysubstitution.
3. Aromatic compounds less reactive than benzene do not undergo Friedel-Crafts alkylation reaction.
4. Aniline $C_6H_5NH_2$ and its derivatives do not undergo Fridel-Crafts alkylation reaction.
5. Aromatic halides cannot be used instead of the alkyl halides in a Fridel-Crafts alkylation reaction.

Assignment No. 3

Draw the structure and name the products in each reaction below.

a) benzene $\xrightarrow{\text{1-chloro propane, } BF_3}$

SIP No. 17
Tape 1 - Work Sheet

Assignment No. 3 (continued)

b) ethyl benzene $\xrightarrow{\text{2-bromo-3,3-dimethyl butane, } AlCl_3}$

c) nitrobenzene $\xrightarrow{\text{ethyl chloride, } AlCl_3}$

d) aniline $\xrightarrow{\text{ethanol, acid}}$

e) toluene $\xrightarrow{\text{isobutanol, acid}}$

f) isopropyl benzene $\xrightarrow{\text{propene, acid}}$

g) benzene $\xrightarrow{CH_2Cl_2, AlCl_3}$

h) toluene $\xrightarrow{CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}Cl, AlCl_3}$

Assignment No. 4

Identify the reagents required for the synthesis of the following compounds from benzene.

a) 1,2-diphenyl ethane

b) diphenyl methane

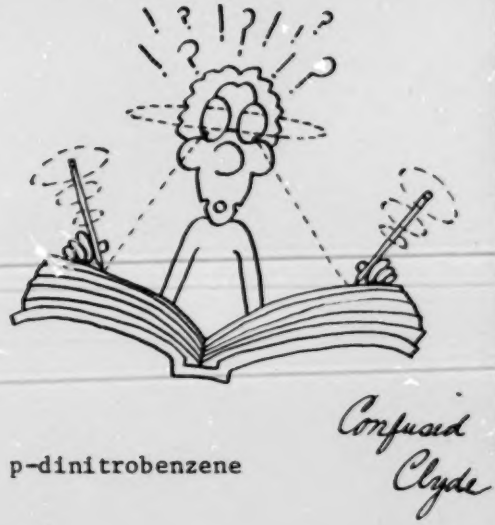
c) p-n-butyl toluene

d) p-diisopropyl benzene

e) p-nitrotoluene

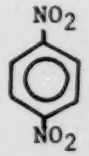
f) p-ethyl benzenesulfonic acid

SIP No. 17
Tape 1 - Work Sheet

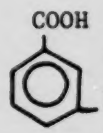


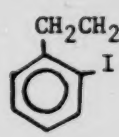
Assignment No. 5

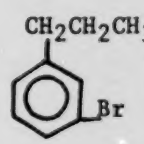
Confused Clyde was asked to complete a number of reactions, name the products and draw their structure. His answer is given below. Rectify his state of confusion.

a) benzene $\xrightarrow{HNO_3, H_2SO_4}$ $\xrightarrow{HNO_3, H_2SO_4}$  p-dinitrobenzene

b) benzene $\xrightarrow{CH_3Cl,\ AlCl_2}$ $\xrightarrow{Br_2, Fe}$ $\xrightarrow{\text{hot } KMnO_4}$ m-bromobenzoic acid

c) benzene $\xrightarrow{CH_3Cl,\ AlCl_3}$ $\xrightarrow{\text{hot } KMnO_4}$ $\xrightarrow{Br_2, Fe}$  m-bromo-benzoic acid

d) benzene $\xrightarrow{\text{propene, acid}}$ $\xrightarrow[CF_3\ COOH]{Tl(OOCCF_3)_3}$ $\xrightarrow{KI}$  o-iodopropylbenzene

e) benzene $\xrightarrow{CH_3CH_2\overset{O}{\overset{\|}{C}}-Cl, AlCl_3}$ $\xrightarrow{Br_2, Fe}$ $\xrightarrow{Zn(Hg)\text{ acid}}$  m-bromo- n-propyl benzene

SIP No. 17
Tape 1 - Work Sheet

Assignment No. 6

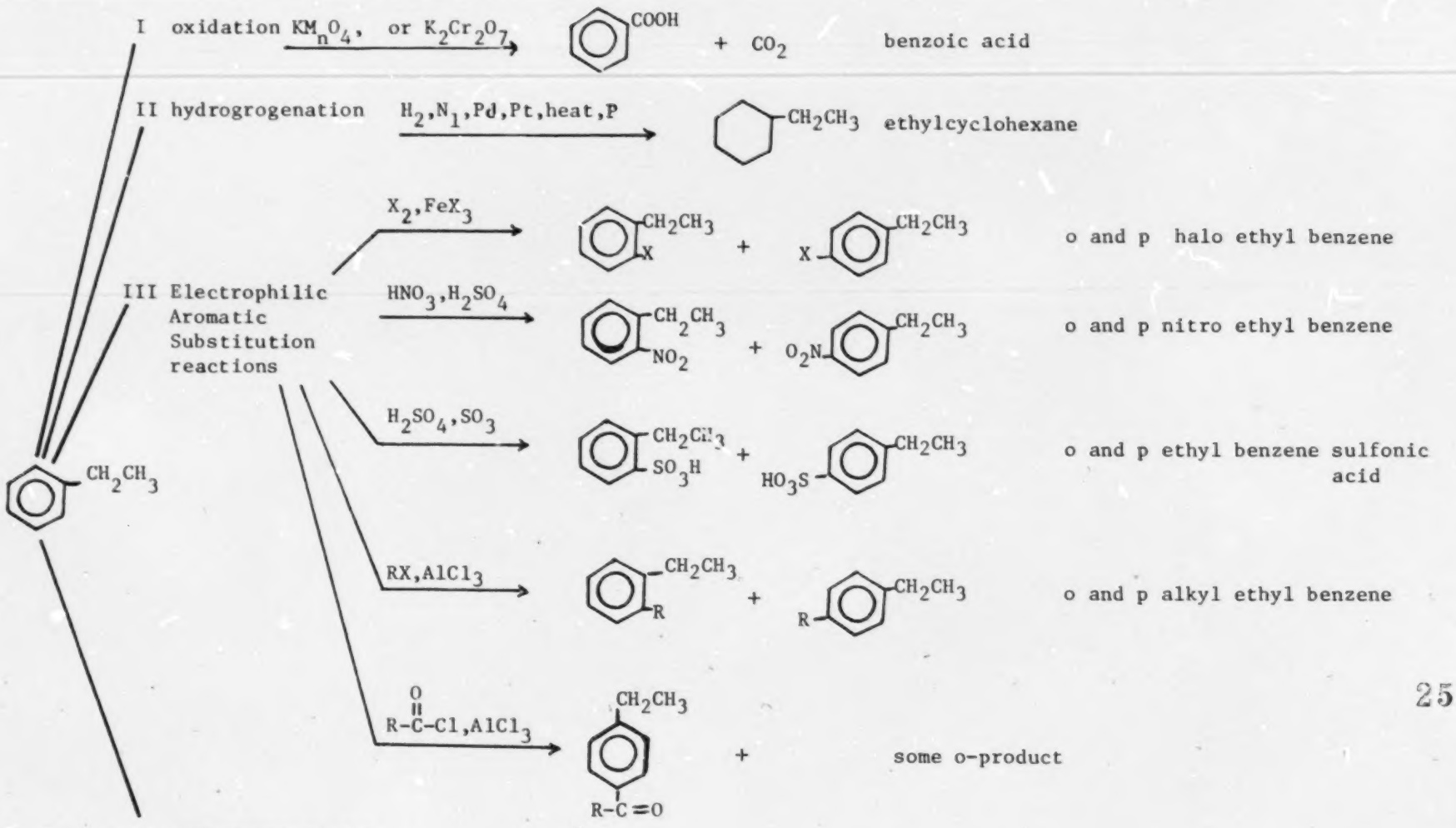
Write the step-by-step mechanism for the reaction of benzene with:
a) 3-methyl-2-butanol and b) 3,3-dimethyl-1-butene in presence of an acid.

Assignment No. 7

Why is polysubstitution a complicating factor in Friedel-Crafts alkylation but not in aromatic nitration, sulfonation, or halogenation?

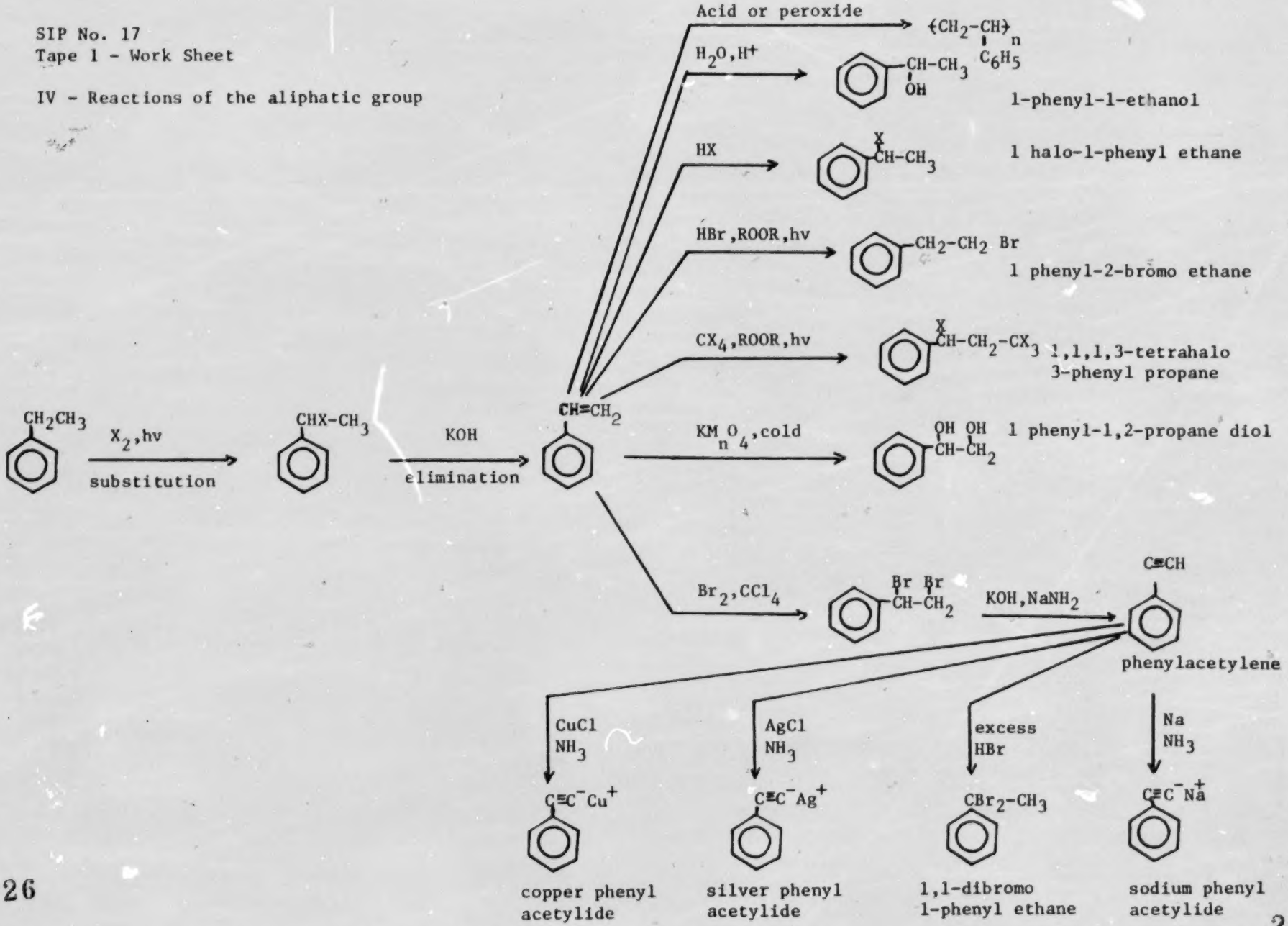
SIP No. 17
Tape 1 - Work Sheet

Example No. 4 - Reactions of Arenes



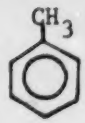
SIP No. 17
Tape 1 - Work Sheet

IV - Reactions of the aliphatic group



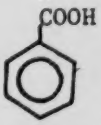
SIP No. 17
Tape 1 - Work Sheet

Example No. 5 - Oxidation of arenes as an identification tool

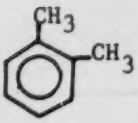


toluene

hot $KMnO_4$
or $K_2Cr_2O_7, H^+$

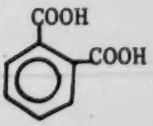


benzoic acid M.P. 127°

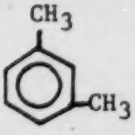


o-xylene

hot $KMnO_4$
or $K_2Cr_2O_7, H^+$

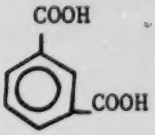


phthalic acid M.P. 231°

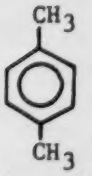


m-xylene

hot $KMnO_4$
or $K_2Cr_2O_7, H^+$

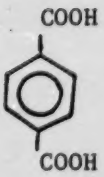


Isophthalic acid M.P. 348°



p-xylene

hot $KMnO_4$
or $K_2Cr_2O_7, H^+$

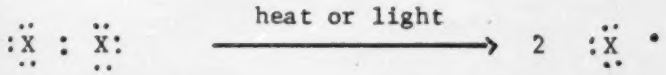


Terephtalic acid M.P. 300°

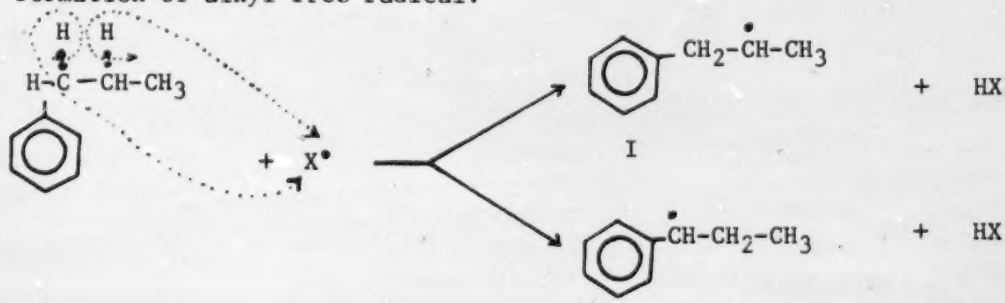
SIP No. 17
Tape 1 - Work Sheet

Example No. 6 - Free Radical Halogenation of Arenes

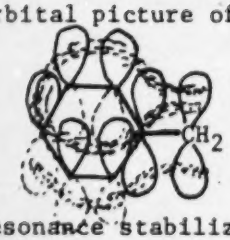
Step 1 - homolytic cleavage of the halogen molecule - X atom is produced



Step 2 - attack of the halogen atom on the alkyl chain in the arene and the formation of alkyl free radical.

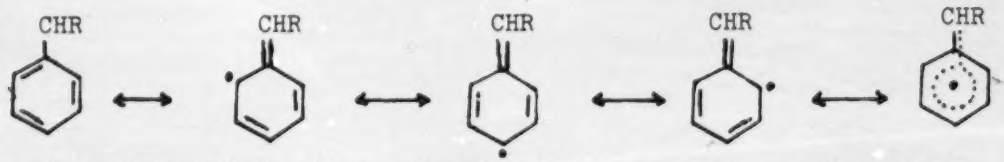


I. Orbital picture of the benzylic free radical.



the odd electron is DELOCALIZED over the entire ring. The π clouds contain 7 electrons

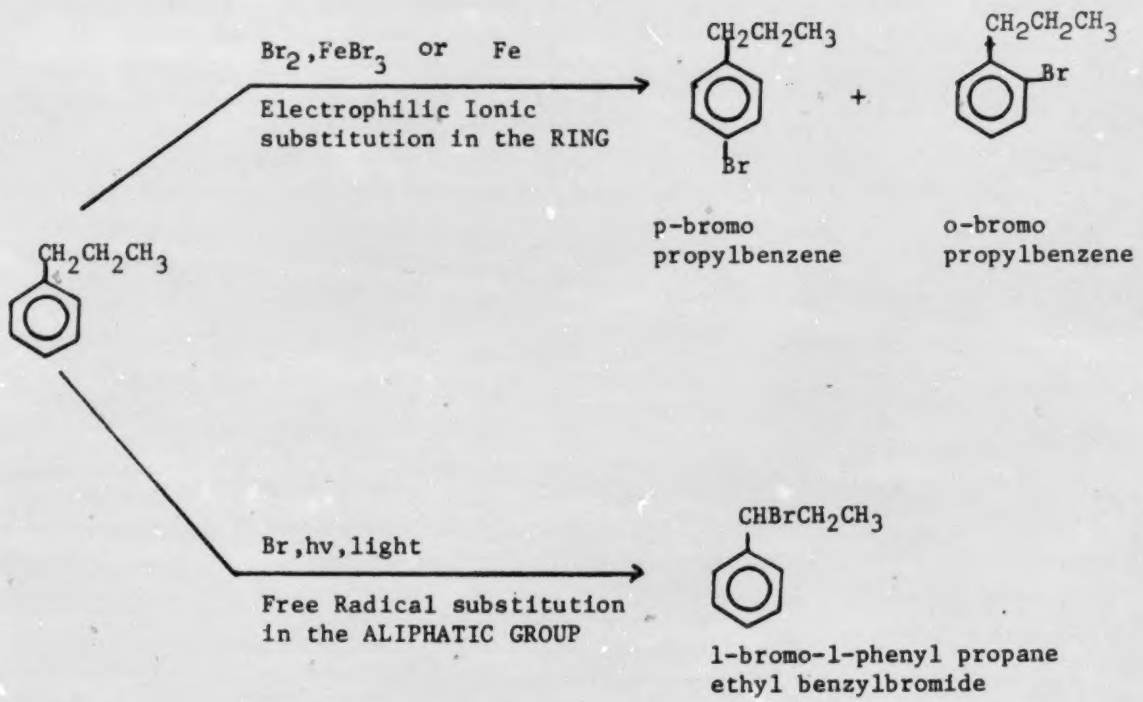
II. Resonance stabilization of the benzylic free radical



Step 3 - abstraction of the halogen atom and the formation of the halide

SIP No. 17
Tape 1 - Work Sheet

Example No. 7 - Halogenation of Arenes



SIP No. 17
Tape 1 - Work Sheet

Assignment No. 8

a) Write all the resonance structures for diphenylmethyl free radical.

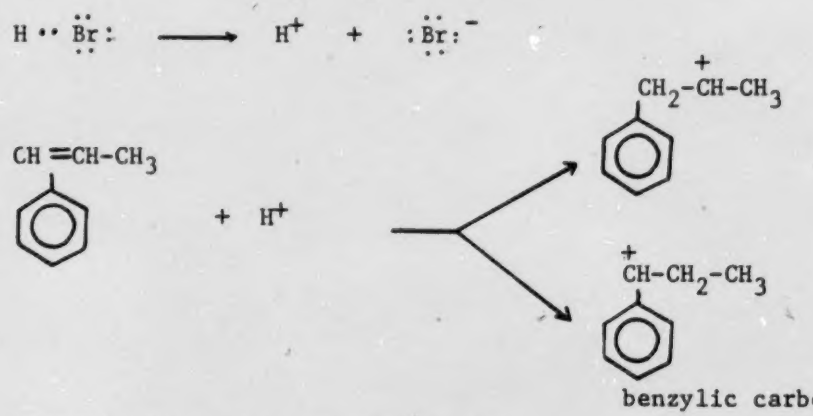
b) Compare the relative stabilities of benzyl free radical, diphenyl methyl free radical and triphenyl methyl free radical.

c) Use the orbital picture to explain and support your answer in b).

SIP No. 17
Tape 1 - Work Sheet

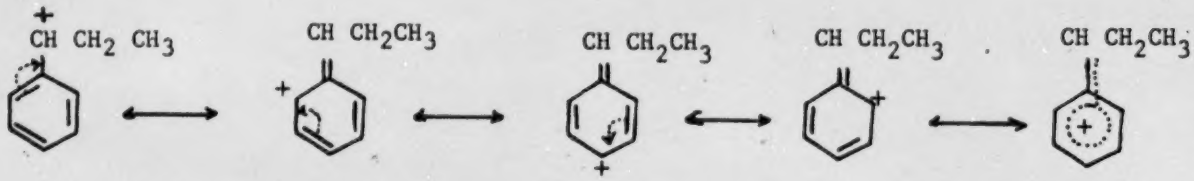
Example No. 8 - Addition of HBr - Mechanism

Step 1 - addition of the H^+ acid formation of the carbonium ion

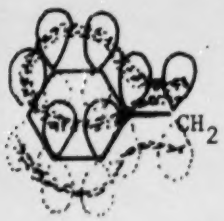


benzylic carbonium ion

Resonance stabilization of the carbonium ion.



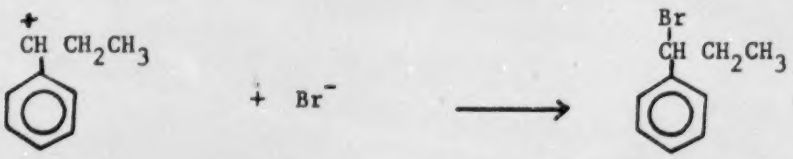
Orbital picture of the benzylic carbonium ion.



the positive charge is DELOCALIZED over the entire ring.

The π clouds contain 6 electrons only.

Step 2 - addition of the bromide anion to the benzylic carbonium ion



1-bromo-1-phenylpropane

SIP No. 17
Tape 1 - Work Sheet

Assignment No. 9

Write the step-by-step mechanism for the peroxide catalyzed addition of HBr to 1-phenyl-1-propene. Draw the resonance structures to explain the stability of the intermediate species.

SIP No. 17
Tape 1 - Work Sheet

Assignment No. 10

Draw the structures and name the products in the following reactions:

a) 1-phenyl-2-butene $\xrightarrow{H_2O,\text{acid}}$

b) 1-phenyl-1-propene $\xrightarrow{\text{bromoform, peroxide, light}}$

c) 2-phenyl-2-butene $\xrightarrow{HCl}$

d) phenyl acetylene $\xrightarrow{\text{excess HBr}}$

e) 2-phenyl-2-butene $\xrightarrow{Cl_2,H_2O}$

f) 1-phenyl propene $\xrightarrow{\text{peroxide, light}}$

g) 1-phenyl-2-butene $\xrightarrow{HBr}$

h) 1-phenyl propene $\xrightarrow{H_2,Pt}$

SIP No. 17
Tape 1 - Work Sheet

i) 1-phenyl propene $\xrightarrow{H_2Pt,Ni,heat,pressure}$

j) phenyl acetylene $\xrightarrow{AgNO_3}$

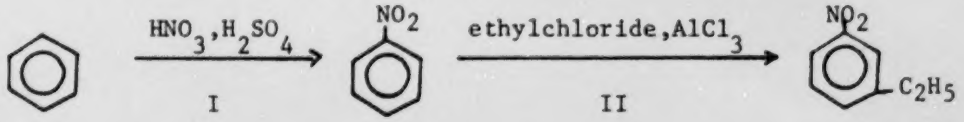
k) 2-methyl-3-phenyl-2-pentene $\xrightarrow{KM_nO_4,aq}$

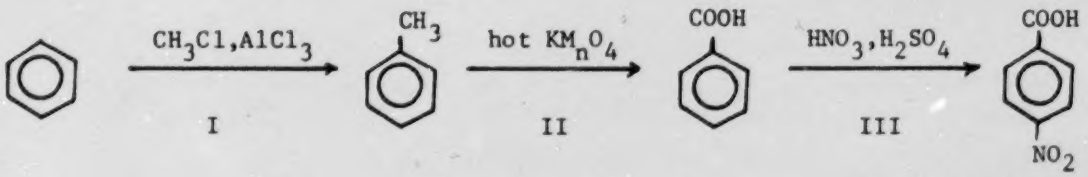
l) 1-phenyl-3-hexene $\xrightarrow{O_3H_2O,Zn}$

Inert Irma

Assignment No. 11

Inert Irma was asked to show all the steps in the multisynthetic scheme for the synthesis of a) m-nitroethyl benzene, b) p-nitrobenzoic acid and c) 2-iodo-1,4,diethyl benzene. Her answer is given below. Examine it thoroughly and supply any necessary corrections.

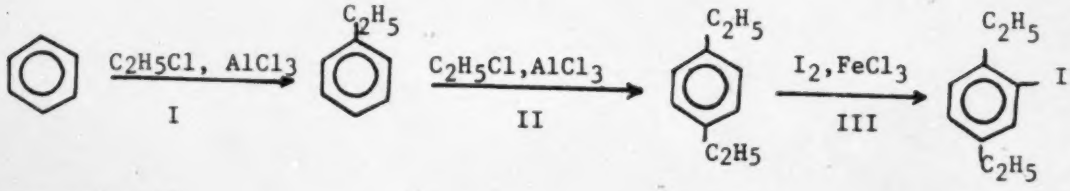
a) 

b) 

SIP No. 17
Tape 1 - Work Sheet

Assignment No. 11 (continued)

c)



Assignment No. 12

Identify all the steps in the laboratory synthesis of the following compounds from benzene:

a) 2-phenyl propene

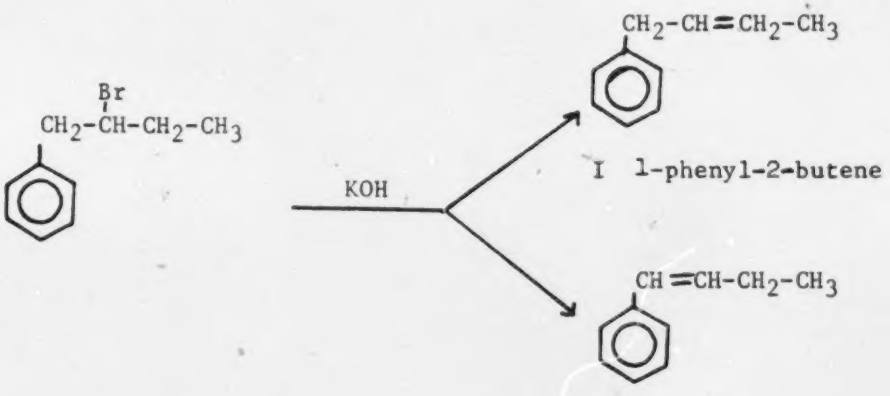
b) 3-phenylpropene

c) p.p' dinitrodiphenylmethane

d) 1-phenyl-1-butanol

SIP No. 17
Tape 1 - Work Sheet

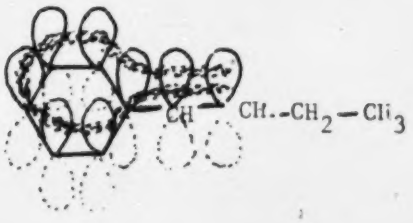
Example No. 9 - Elimination reaction of 1-phenyl-2-bromobutane



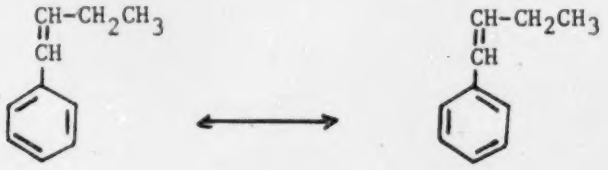
I 1-phenyl-2-butene

II 1-phenyl-1-butene

I. orbital picture of 1-phenyl-1-butene



II. resonance structures of 1-phenyl-1-butene



SIP No. 17
Tape 1 - Work Sheet

Assignment No. 13

Arrange in order of ease of dehydration, alcohols in each group below:

I. a) 1-phenyl-2-propanol

b) 1-phenyl-1-propanol

c) 1,1-diphenyl-1-propanol

II. a) 2-phenyi 1-butanol

b) 2-phenyl-2-butanol

c) 1-phenyl-1-butanol

Assignment No. 14

The heats of hydrogenation of the stereoisomeric 1,2-diphenyl ethylenes are: cis - 26.3 kcal; trans-20.6 kcal. Which isomer is the more stable?

Assignment No. 15

The three xylenes are obtained as a mixture from the distillation of coal tar. Propose a viable chemical method for their identification after separation.

SIP No. 17
Tape 1 - Work Sheet

Assignment No. 16

Outline all steps in a laboratory synthesis of the following compounds from benzene:

a) cis-1-phenyl propene

b) trans-1-phenyl propene

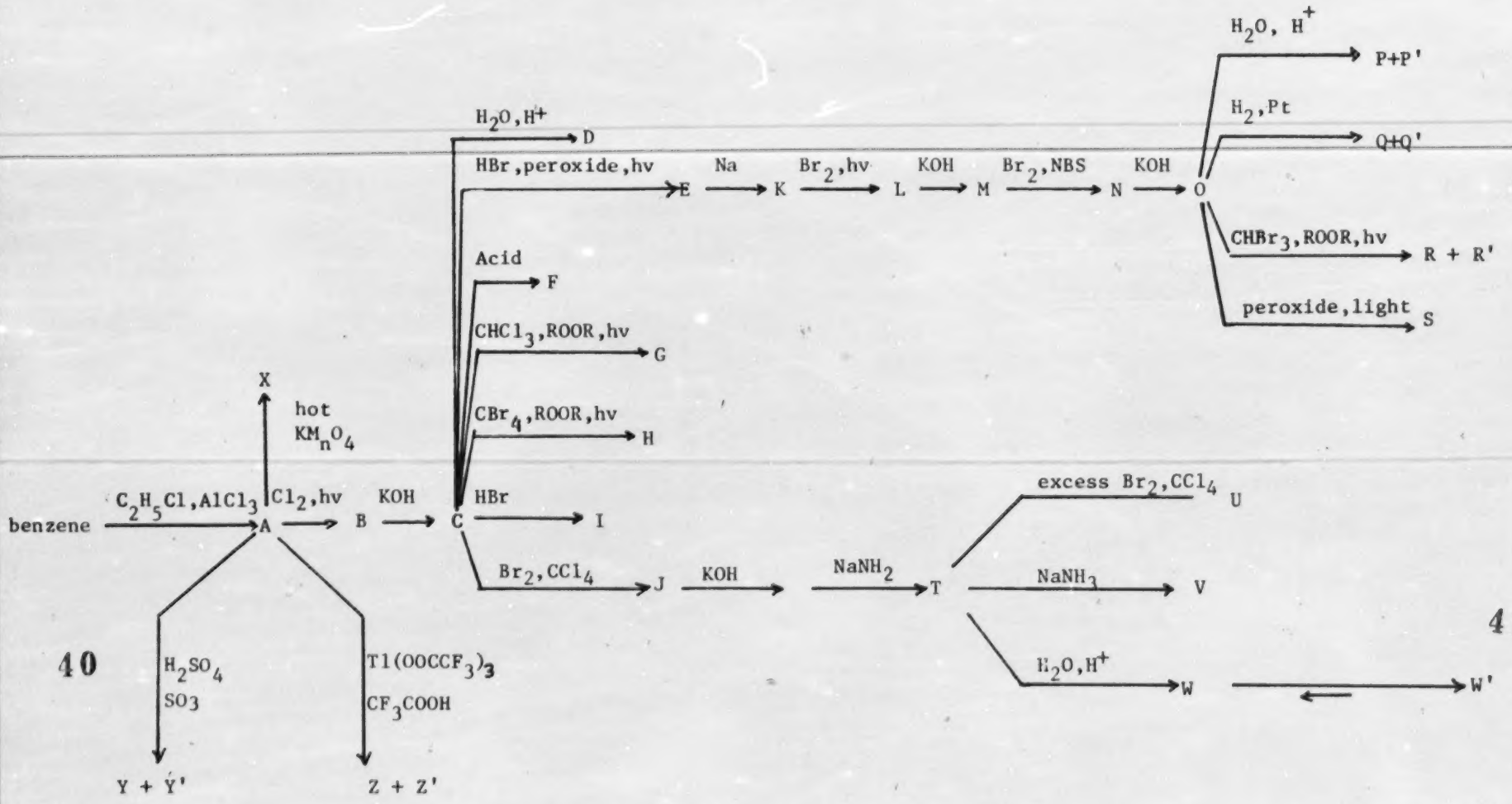
c) p-nitrostyrene

d) p-bromobenzylbromide

SIP No. 17
Tape 1 - Work Sheet

Assignment No. 17

Draw the structures and name compounds A through Z in the multisynthetic scheme below:



40

41

Self Instructional Package No. 17
Tape 1 - Answer Sheet

ARENES

Assignment No. 1

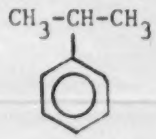
a) diphenyl acetylene

b) 4-methyl-4-phenyl-2-pentene

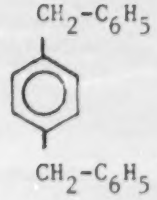
c) 2-benzyl butane

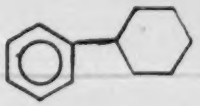
d) 2,4-dimethyl-2-phenyl-3-benzyl hexane

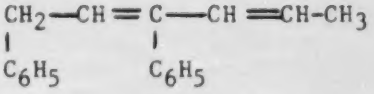
Assignment No. 2

a) 

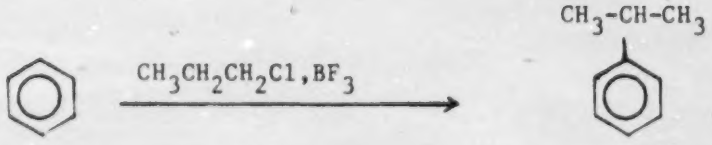
b) $C_6H_5-CH_2-C_6H_5$ or $(C_6H_5)_2CH_2$

c) 

d) 

e) 

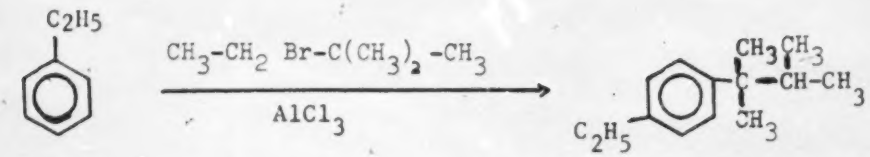
Assignment No. 3

a) 

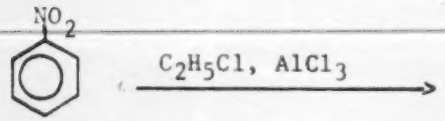
isopropylbenzene

SIP No. 17
Tape 1 - Answer Sheet

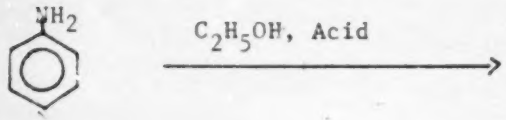
Assignment No. 3 (continued)

b) 

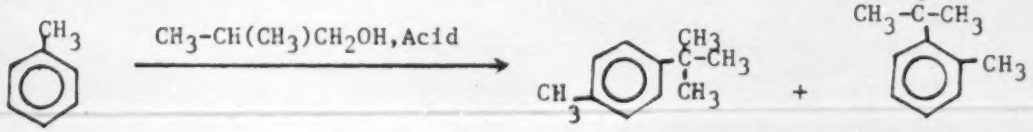
2-methyl-3- (p-ethylphenyl) butane

c) 

N.R.

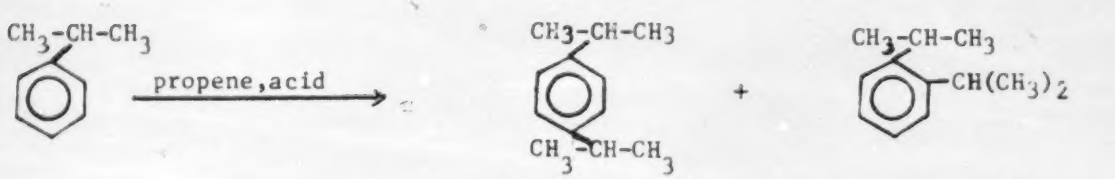
d) 

N.R.

e) 

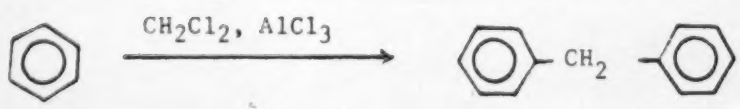
p-t-butyl toluene

o-t-butyl toluene

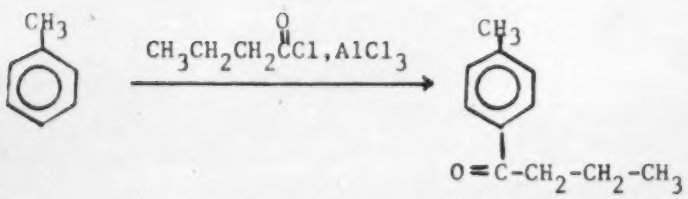
f) 

p-diisopropylbenzene

o-diisopropylbenzene

g) 

diphenylmethane

h) 

SIP No. 17
Tape 1 - Answer Sheet

Assignment No. 4

a) benzene $\xrightarrow{CH_2ClCH_2Cl\ AlCl_3}$ $C_6H_5\ CH_2\ CH_2C_6H_5$

b) benzene $\xrightarrow{CH_2\ Cl_2,\ AlCl_3}$ $(C_6H_5)_2CH_2$

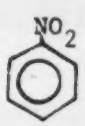
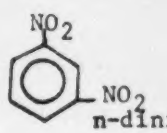
c) benzene $\xrightarrow{CH_3Cl,AlCl_3}$ toluene $\xrightarrow{CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}Cl,AlCl_3}$ $\xrightarrow{Zn(Hg)Acid}$ p-n-butyl toluene

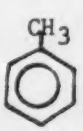
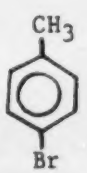
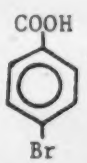
d) benzene $\xrightarrow{CH_3\ CHCl\ CH_3,AlCl_3}$ $\xrightarrow{CH_3\ CHCl\ CH_3,AlCl_3}$ p-diisopropylbenzene

e) benzene $\xrightarrow{CH_3Cl,AlCl_3}$ $\xrightarrow{HNO_3,H_2SO_4}$ p-nitrotoluene

f) benzene $\xrightarrow{\text{ethyl bromide, } BF_3}$ $\xrightarrow{H_2SO_4,SO_3}$ p-ethylbenzenesulforic acid

Assignment No. 5

a) benzene $\xrightarrow{HNO_3,H_2SO_4}$  $\xrightarrow{HNO_3,H_2SO_4}$  n-dinitrobenzene

b) benzene $\xrightarrow{CH_3Cl,AlCl_3}$  toluene $\xrightarrow{Br_2,Fe}$  p-bromotoluene (+ o-bromotoluene) $\xrightarrow{\text{hot } KMnO_4}$  p-bromobenzoic acid

c) correct

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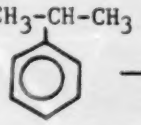
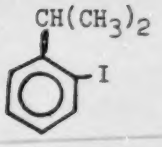
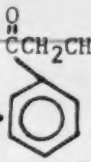
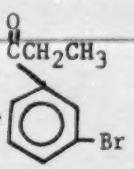
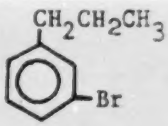
Tape 1 - Answer Sheet

Assignment No. 5 (continued)

d) benzene $\xrightarrow{\text{propene, acid}}$  $\xrightarrow[CF_3\ COOH]{Tl(OOCCF_3)_3}$ $\xrightarrow{KI}$ 

isopropylbenzene

o-iodoisopropyl benzene

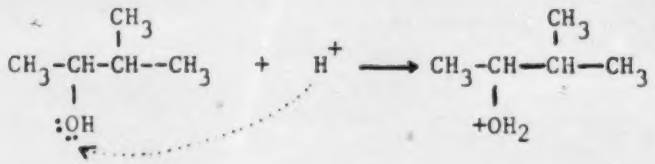
e) benzene $\xrightarrow[AlCl_3]{CH_3CH_2C(=O)Cl}$  $\xrightarrow{Br,\ Fe}$  $\xrightarrow{Zn(Hg)\ acid}$ 

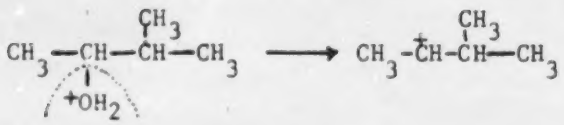
m-bromopropyl benzene

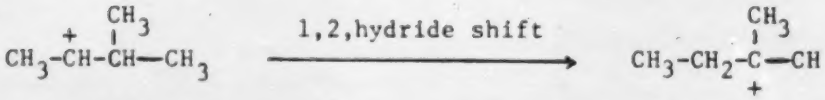
Assignment No. 6

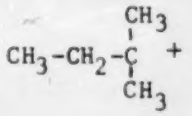
I Formation of the attacking species:

a) 3-methyl-2-butanol







the attacking species R^+ is 

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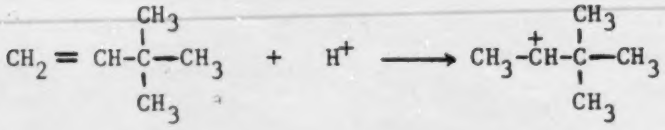
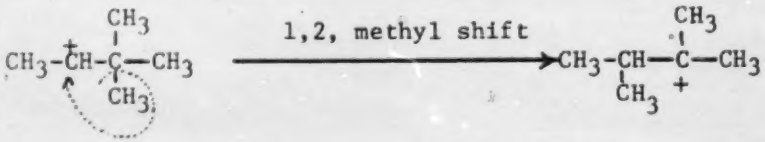
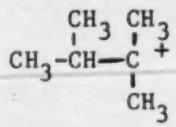
Assignment No. 6

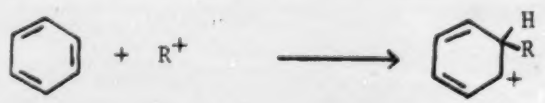
b) 3,3-dimethyl-1-butene





The attacking species R^+ is 

Step 1 - Attack of the electrophile on the benzene ring



Resonance stabilization of the intermediate carbonium ion

Step 2 - Recovery of the aromatic structure and the regeneration of the catalyst

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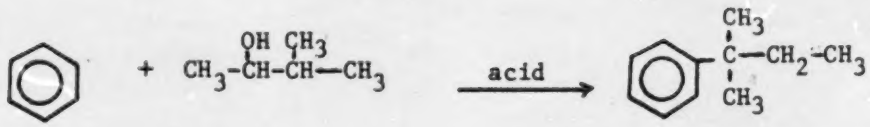
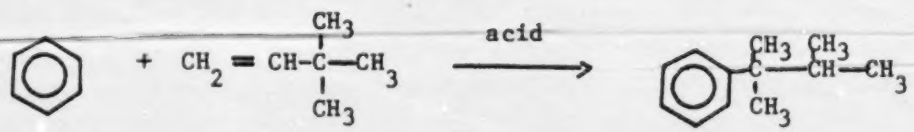
Overall reactions:



2-methyl-2-phenyl butane



2,3-dimethyl-2-phenyl butane

Assignment No. 7

An arene obtained in a Friedel Crafts alkylation reaction is more reactive than benzene itself and will readily undergo further substitution.

Nitrobenzene, halobenzene and benzenesulfonic acid are less reactive than benzene and will not readily undergo further substitution.

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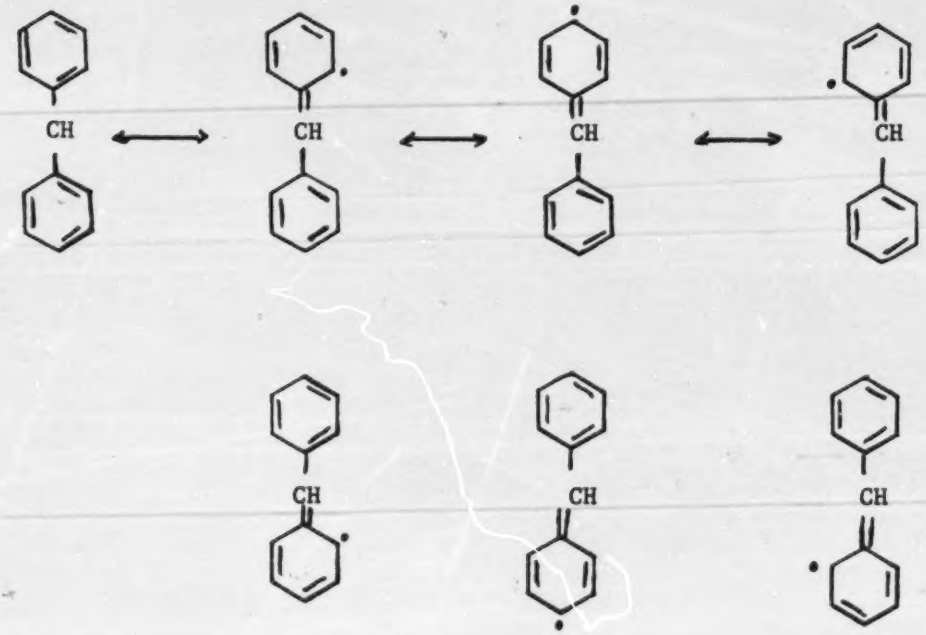
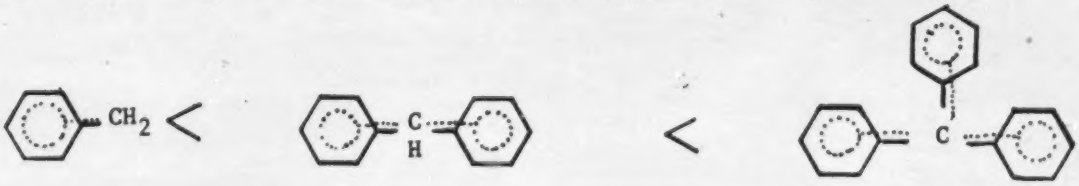
Tape 1 - Answer Sheet

Assignment No. 8

Resonance structures of the diphenyl methyl free radical



Triphenyl methyl free radical is more stable than the diphenyl methyl free radical which is more stable than the benzylic free radical.



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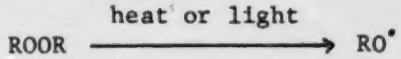
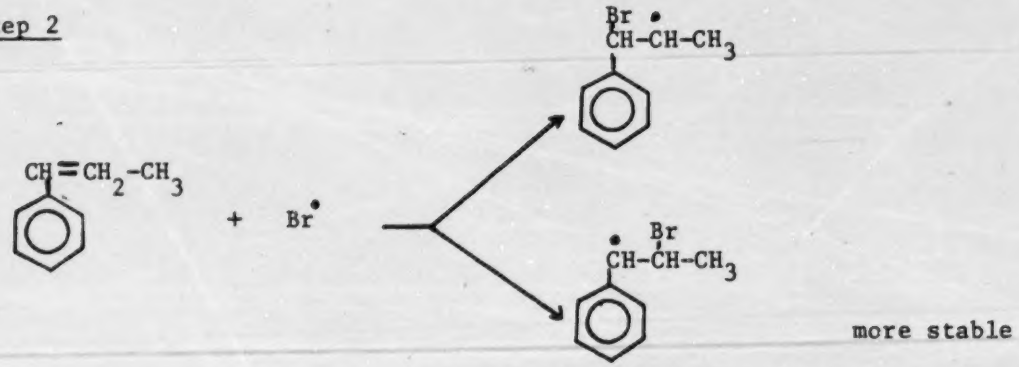
Assignment No. 9

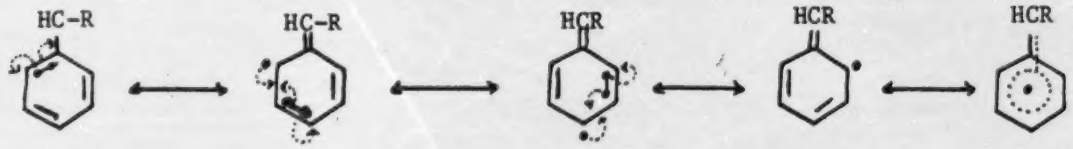
Step 1



Step 2



Resonance stabilization of the intermediate free radical:



Step 3

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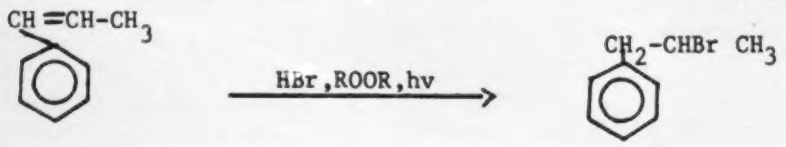
Overall reaction:



Assignment No. 10

a) $C_6H_5-CH(CH_2)-CH=CH-CH_3 \xrightarrow{H_2O,\ acid} C_6H_5-CH(OH)-CH_2-CH_2-CH_3$ 1-phenyl-1-butanol

b) $C_6H_5-CH=CH-CH_3 \xrightarrow{CHBr_3,ROOR,hv} C_6H_5-CH(CH_2)-CH(CBr_3)-CH_3$ 1,1,1-tribromo-2-methyl--3-phenyl butane

c) $CH_3-C(C_6H_5)=CH-CH_3 \xrightarrow{HCl} CH_3-C(Cl)(C_6H_5)-CH_2-CH_3$ 2-chloro-2-phenyl butane

d) $C_6H_5-C\equiv CH \xrightarrow{excess\ HBr} C_6H_5-C(Br)_2-CH_3$ 1,1-dibromo-1-phenyl ethane

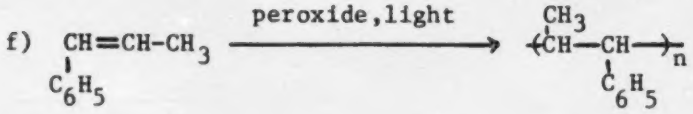
e) $CH_3-C(C_6H_5)=CH-CH_3 \xrightarrow{Cl_2,H_2O} CH_3-CCl(C_6H_5)-CHCl-CH_3 + CH_3-C(OH)(C_6H_5)-CHCl-CH_3$

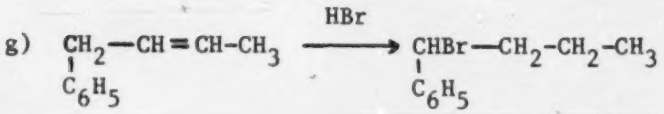
2,3-dichloro-2-phenyl butane

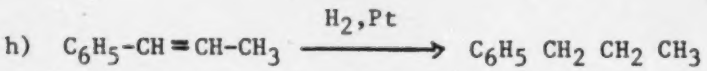
3-chloro-2-phenyl 2-butanol

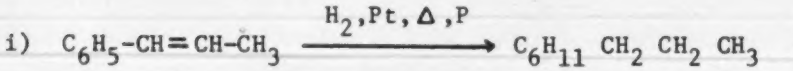
SIP No. 17
Tape 1 - Answer Sheet

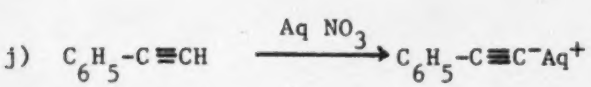
Assignment No. 10 (continued)

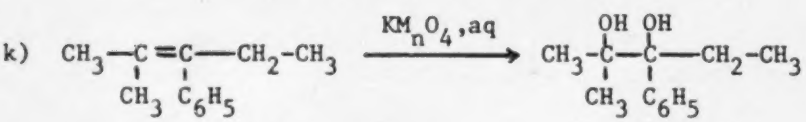
f) 

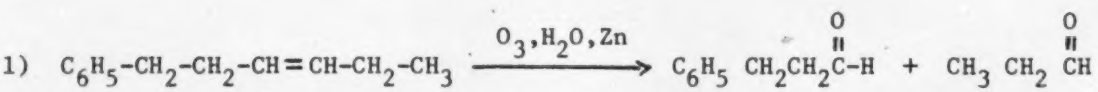
g)  1-bromo-1-phenyl butane

h)  propylbenzene

i)  propyl cyclohexane

j)  silver phenylacetylide

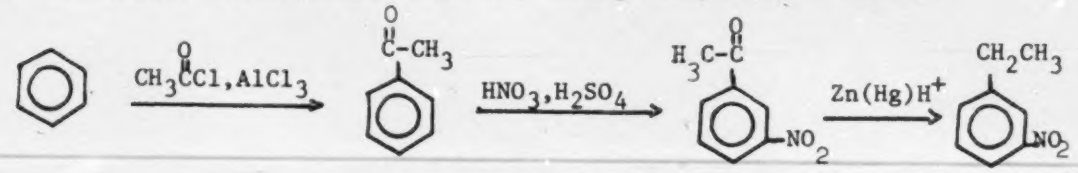
k) 

l) 

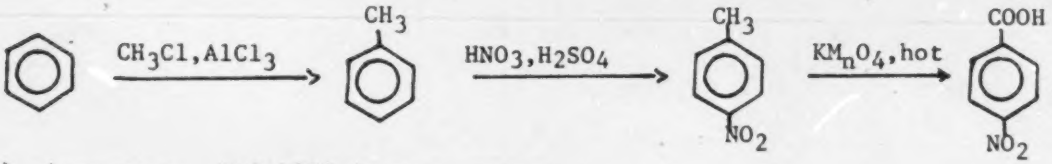
SIP No. 17
Tape 1 - Answer Sheet

Assignment No. 11

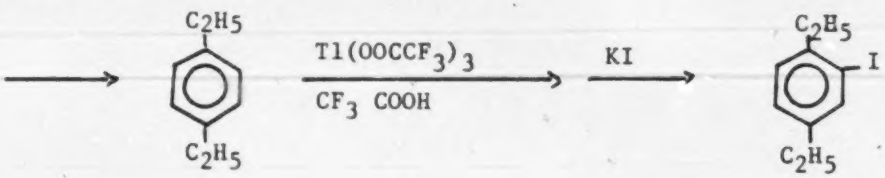
a) incorrect. Nitrobenzene does not undergo alkylation reaction.



b) incorrect. COOH group is a m-director.



c) incorrect. Step III is not correct.



Assignment No. 12

a) benzene → propene, acid → $CH_3CH\ CH_3$ → Br_2, hv → KOH → $CH_3-C=CH_2$

b) benzene → 3-chloro propene, $AlCl_3$ → $CH_2-CH\ CH_2$

c) benzene → CH_2Cl_2, $AlCl_3$ → CH_2 → HNO_3, H_2SO_4 → NO_2, CH_2, $_2ON$

d) benzene → $CH_3\ CH_2\ CH_2\ COCl$, $AlCl_3$ → $C-(CH_2)_2CH_3$ → Zn(Hg) Acid → $CH_2(CH_2)_2CH_3$ → Br_2, hv → $CHBrCH_2CH_2CH_3$ → KOH → $CH=CHCH_2CH_3$ → H_2O, acid → $OH\ CH_2CH_2CH_2CH_3$

SIP No. 17
Tape 1 - Answer Sheet

Assignment No. 13

I c > b > a

II b > c > a

Assignment No. 14

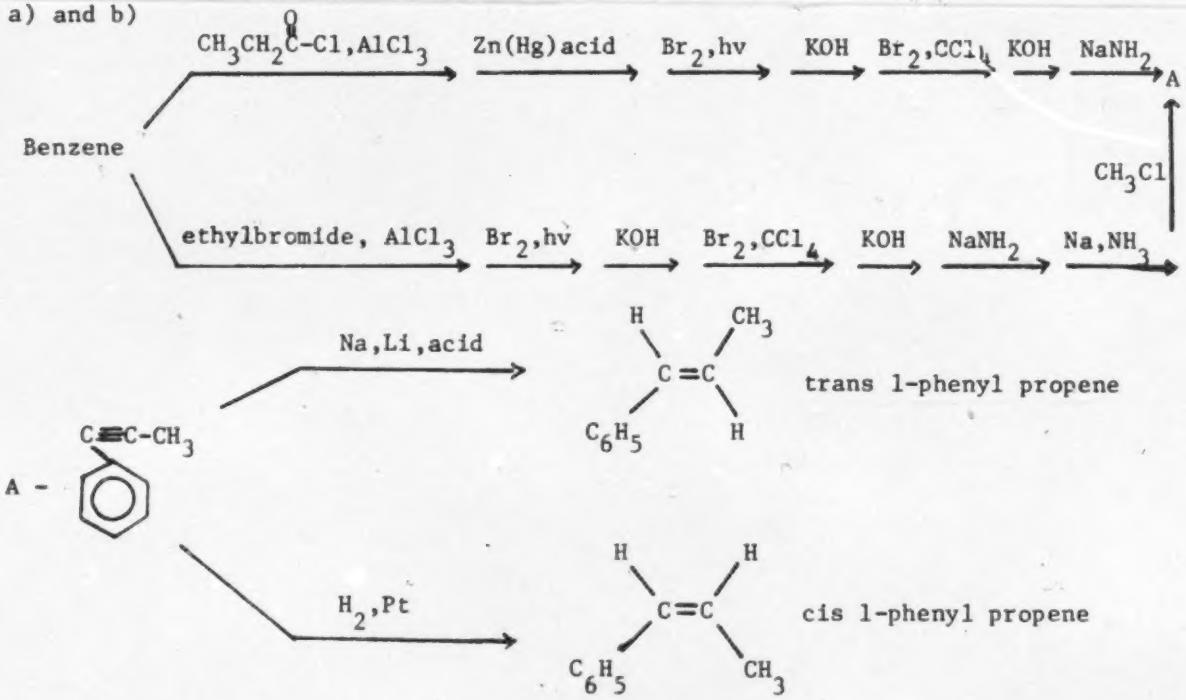
trans stibene

Assignment No. 15

Conversion of liquid xylenes into solid benzene dicarboxylic acids via oxidation with hot $KMnO_4$ or $K_2Cr_2O_7$ and acid. Identification of the solid acids via their melting points.

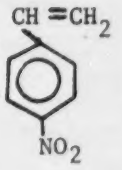
Assignment No. 16

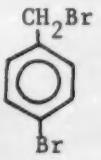
a) and b)



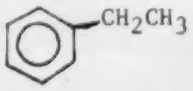
SIP No. 17
Tape 1 - Answer Sheet

Assignment No. 16 (continued)

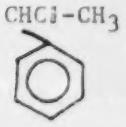
c) benzene $\xrightarrow[\text{I}]{C_2H_5Cl,AlCl_3}$ $\xrightarrow[\text{II}]{HNO_3,H_2SO_4}$ $\xrightarrow[\text{III}]{Br_2,h\nu}$ $\xrightarrow[\text{IV}]{KOH}$ 

d) benzene $\xrightarrow[\text{I}]{CH_3Cl,AlCl_3}$ $\xrightarrow[\text{II}]{Br_2,Fe}$ $\xrightarrow[\text{III}]{Br_2,h\nu}$ 

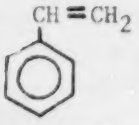
Assignment No. 17



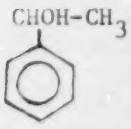
ethylbenzene



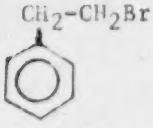
B - 1-chloro-1-phenylethane



styrene (phenylethylene)



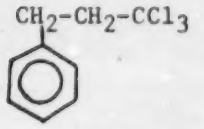
1-phenyl-1-ethanol



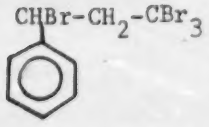
1-phenyl-2-bromo ethane

F - $-(CH_2-\underset{\underset{C_6H_5}{|}}{CH}-CH_2)_n-$

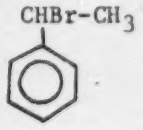
polystyrene

G - 

1,1,1-trichloro-3-phenyl propane

H - 

1,1,1,3-tetrabromo-3-phenyl propane

I - 

1-bromo-1-phenylethane

SIP No. 17
Tape 1 - Answer Sheet

Assignment No. 17 (continued)

J -

1,2-dibromo-1-phenyl ethane

K - $CH_2(C_6H_5)-CH_2-CH_2-CH_2(C_6H_5)$

1,4-diphenyl butane

L - $CHBr-CH_2-CH_2-CH_2$ (C_6H_5 on each CH)

1,4-diphenyl-1-bromo butane

M - $CH=CH-CH_2-CH_2$ (C_6H_5 on each CH)

1,4-diphenyl-1-butene

N - $CH=CH-CHBr-CH_2$ (C_6H_5 on each CH)

3-bromo-1,4-diphenyl
1-butene

O - $CH=CH-CH=CH$ (C_6H_5 on each CH)

1,4-diphenyl-1,3-butadiene

P - $CHOH-CH_2-CH=CH$ (C_6H_5 on each CH)

1,4-diphenyl-1-butene-4-ol

P' $CHOH-CH=CH-CH_2$ (C_6H_5 on each CH)

1,4-diphenyl-2-butene-1-ol

Q - $CH=CH-CH_2-CH_2$ (C_6H_5 on each CH)

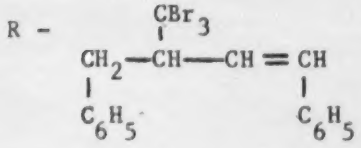
1,4-diphenyl-1-butene

Q' $CH_2-CH=CH-CH_2$ (C_6H_5 on each CH)

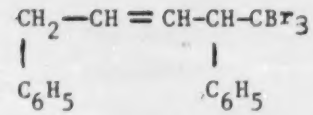
1,4-diphenyl-2-butene

SIP No. 17
Tape 1 - Answer Sheet

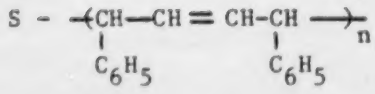
Assignment No. 16 (continued)

R - 

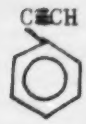
4,4,4-tribromo-4-benzyl-1-phenyl-1-butene

R' 

5,5,5-tribromo-1,4-diphenyl-2-pentene

S - 

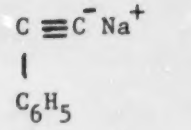
poly 1,4-diphenyl butadiene

T - 

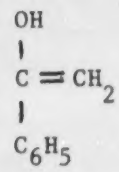
phenylacetylene

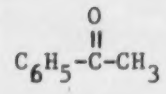
U - $C_6H_5-CBr_2-CHBr_2$

1,1,2,2-tetrabromo-1-phenyl acetylene

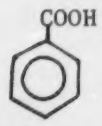
V - 

sodium phenylacetylide

W - 

W' 

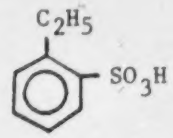
phenyl methyl ketone

X - 

benzoic acid

Y -

p-ethyl benzene sulfonic acid

Y' 

o-ethylbenzene sulfonic acid